Scientific report for support of the short visit by Marion Bauer at ISIS:

Micropore Collapse in Bulk Amorphous Solid Water

Purpose of the visit

Even though practically all water ice on Earth is crystalline, in the universe it is mostly amorphous. Amorphous solid water (ASW) accretes onto dust particles in the cold regions of dense interstellar clouds, and its mesoscale structure influences subsequent chemistry that can be occurring during star and planet formation [1a]. ASW is thought to be connected to deeply supercooled liquid water by a glass transition at $T_g \approx 136$ K [1b], and thus not only of astrophysical interest [2], but also a model substance for understanding bulk liquid water [3].

The nature of ASW sensitively depends on its conditions of preparation, which is generally done by water vapour deposition on cold substrates. The surface area and the porosity of ASW samples are strongly influenced by parameters such as the deposition temperature and the angle of incidence in molecular beam experiments [4, 5]. Highest surface area samples, reaching porosities of up to 60% and surface areas of up to 2000 m^2/g, are produced by deposition at lowest temperature (e.g., 10 K) and deposition at angles of around 60° or omni-directional deposition [4]. Also the use of non-baffled, supersonic flow conditions, in which water oligomers rather than water monomers are thought to be deposited, was shown to produce high surface area ASW bulk samples even at 77 K[6]. These high surface area samples have a huge capacity to adsorb gases [2, 7, 8], with BET measurements suggesting they contain a vast number of micropores of up to 18 Å diameter [9a]. Such samples produce tower-like structures of a few cm of length in experiments, as also found in complementary molecular scale MD-simulations at the University of Strathclyde [9b]. In parallel to the neutron work these simulations will focus on the long-time scale process of pore collapse under the deposition and temperature conditions used in the neutron study.

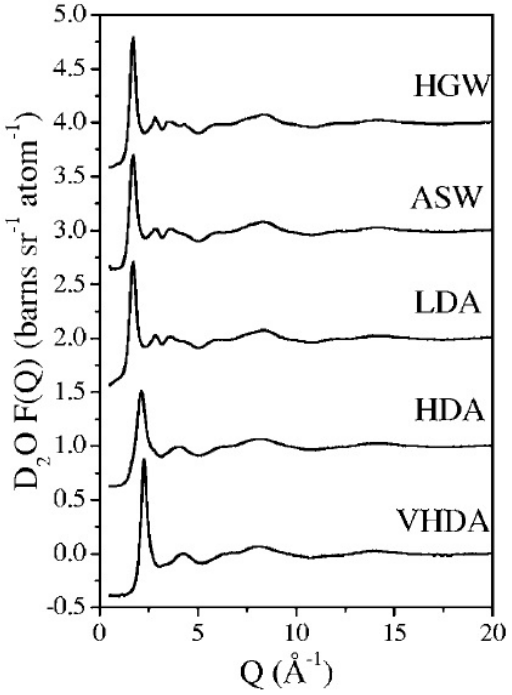

Figure 1: The fully corrected experimentally measured interference differential scattering cross sections F(Q) for VHDA, HDA, LDA, ASW, and HGW ices prepared using D_2O. For clarity the functions are vertically offset by 0, 1.0, 2.0, 3.0, and 4.0 units, respectively (taken from ref. 14).

Upon heating the surface area is reduced dramatically, e.g., to 0.1 m^2/g [10], and the network of micropores was qualitatively suggested to collapse [11-13]. These samples are referred to as annealed ASW and have been studied earlier on SANDALS by isotope substitution neutron diffraction [14]. Annealed ASW samples were shown in these experiments to have the same radial distribution functions as hyperquenched glassy water (HGW), produced by rapid quenching of micron-sized water droplets, and low-density amorphous ice (LDA), produced after pressure-amorphization of hexagonal ice [14] (see Figure 1). However, some volatile molecules such as CO, CO_2 or CH_3OH adsorbed to high-surface ASW samples remain irreversibly trapped inside ASW even after the collapse of the micropore network [15-17], and may induce crystallization to cubic structure clathrate hydrates upon heating to T > 160 K [18-20]. A quantitative understanding of the morphology of micropores has remained elusive, and it is also entirely unknown how deposition details affect mesoscale structuring. The fast acquisition times at NIMROD and the use of bulk (and not thin film) samples provide the unique opportunity to study how the mesoscale structure changes upon annealing in "pure" ASW samples (rather than ASW samples contaminated by adsorbed background gas)[10].

A recent X-ray study conducted at the University of Innsbruck shows a clear difference between unannealed, highly microporous bulk samples and annealed samples at low angles $2\theta<10°$ (see Figure 2). There is a small decrease in the low angle signal after heating the sample for one minute to 115 K (red vs. black trace), and a substantial decrease after heating the sample for another minute to 125 K (green vs. red trace). Further heating for another minute to 135 K (blue vs. green trace) does not cause much further change even though the low angle signal does not disappear entirely. We interpret this change in the low angle signal as reporting a collapsing network of pores as outlined above and estimate from the data an average diameter of the heterogeneities in the network of about 10 Å. However, the X-ray diffraction results do not allow for a detailed analysis of the mesostructure of the ASW sample as a function of temperature. Such an analysis requires the study of D_2O samples on NIMROD to significantly lower Q. This will allow us to take advantage of the unique capability of the instrument to probe the porous mesostructure of a material through a wide Q-range Fourier transform that directly shows, in real-space, the relationship between the inter-molecular connectivity and the resulting nanoscale material morphology [21].

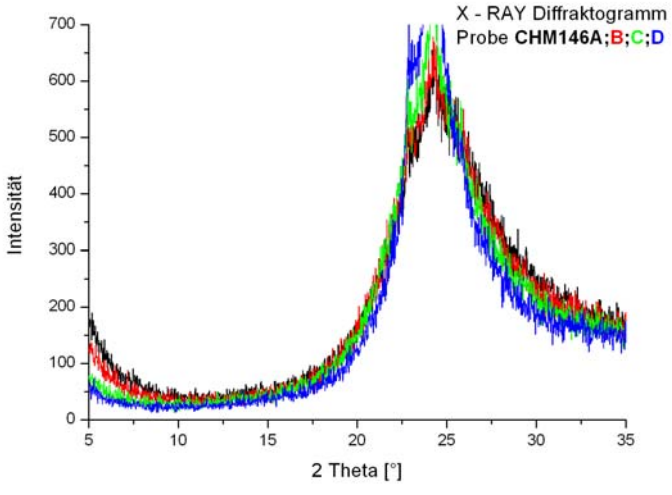

Figure 2: Powder X-ray diffractograms for an ASW sample after deposition at 77 K, storage in liquid nitrogen and transfer to the sample holder kept at 80 K for the transfer. Measurements were done on a Siemens D5000 powder X-ray diffractometer in θ-θ geometry using Cu-$K\alpha_1$ (λ=1.5405 Å) at 80 K measurement temperature. (A, black trace) Without annealing. (B, red trace) After heating for one minute to 115 K. (C, green trace) After heating for one minute to 125 K. (D, blue trace) After heating for one minute to 135 K.

We were granted 3 days of beam time for the experiment RB1210386 on NIMROD at ISIS to study the change of the mesoscale structure of ASW samples in the process of annealing them *in situ* in the temperature range from 80 K to 160 K. At least two people are needed for the work on site so my colleague Christian Mitterdorfer and me applied for a short visit.

Description of the work and results

We stayed at ISIS from May 29th to June 2nd and studied the change in the mesoscale structures using the whole Q-range available at NIMROD and then focus on the kinetics of the micropore network collapse in the low-to-medium Q-range at 0.02 Å^{-1} to 10.0 Å^{-1} by taking advantage of the instrument's high counting rate [22]. We compared four different types of D_2O samples, namely two that are prepared using baffled flow (i.e., background deposition of mainly water monomers) and two prepared using non-baffled line of sight deposition (i.e., direct deposition of water oligomers). For both types of ASW samples we prepared one at high-deposition rate (250 µm/h) and one at low-deposition rate (50 µm/h) in order to also obtain information about the influence of deposition rate on mesoscale structuring. An additional sample type - prepared without any contact of liquid nitrogen using non-baffled line of sight deposition with a medium deposition rate (150 µm/h) - was measured in a front loading cell.

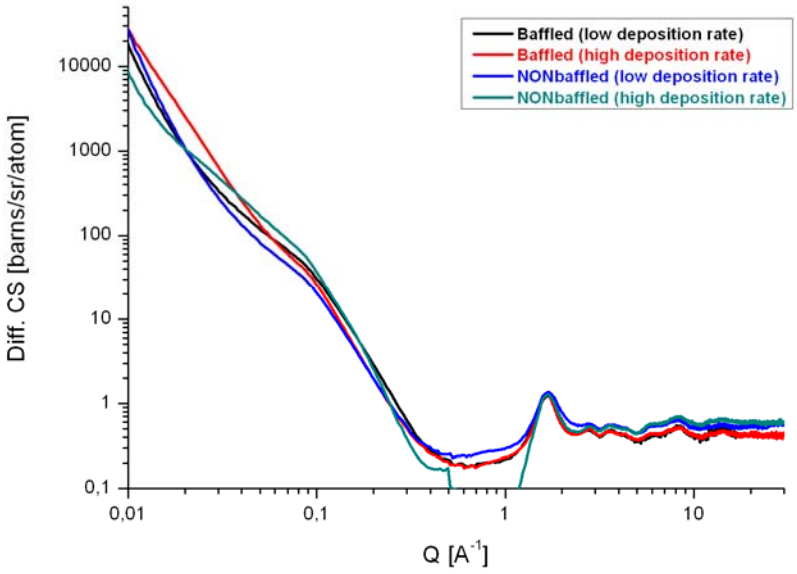

Figure 3: Differential cross section vs. Q space of the data measured at 80 K is shown. The sharp increase to lower Q values is perfectly seen, also the shoulder. This structure arises from the mesoscale structuring of the samples. At Q values > 1Å the structure is identical compared to the earlier measurements at ISIS (see Fig. 1). The minimum in the cyan graph arises from a slightly twisted sample holder.

All samples were first measured isothermal at 80 K and then heated to 160 (170) K while doing *in situ* measurements. In 10 K steps again isothermal runs were performed. Figure 3 shows the results of the measurements at 80 K. The structure at Q values greater 1 is the same compared to the earlier measurements at SANDALS seen in Fig. 1. At low Q values a big increase and a shoulder is seen in all measured

samples. This increase arises from the mesoscale structuring and will give us more details about the pore structure after analyzing the results in detail.
We have done a first analysis and interpretation by displaying the differential data versus r-space (Figure 4). Here, a mutual intermediate pore size, and differing structures of the different samples can be seen.

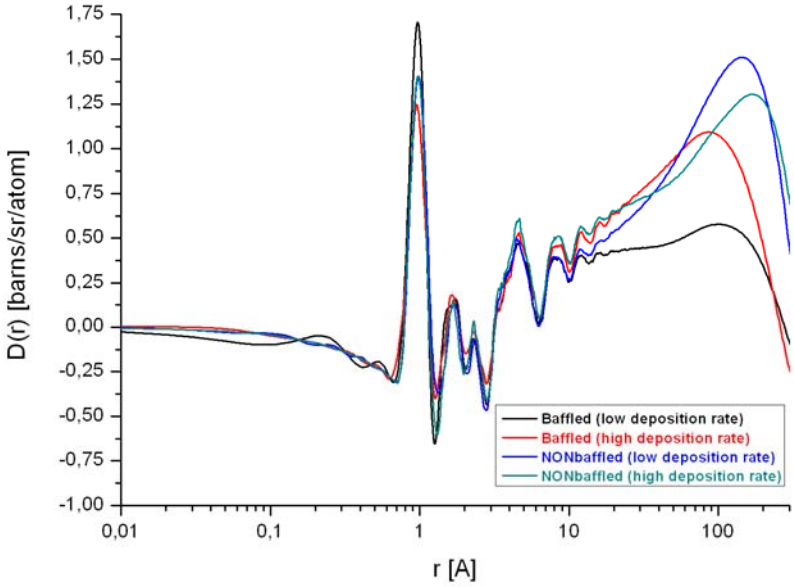

Figure 4: Radial distribution function D(r) vs. r space of the data measured at 80 K is shown. The maximum ~150 Å reflects the averaged pore size.

Future collaborations

As a result of our collaboration discussions we stipulated several new measurements. Within this ideas we plan supplementary experiments at ISIS, e.g. at lower temperatures or with guest molecules in the pores. In addition, a long-term cooperation with Dr. Helen Fraser arises.

Projected Publications

We plan to publish the results from these measurements in the next month; probably two papers can arise from this work.

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